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**PREPARATION OF INGOTS OF URANIUM —
NIOBIUM ALLOY**

U N C L A S S I F I E D

ISC-743

U N I T E D S T A T E S A T O M I C E N E R G Y C O M M I S S I O N

PREPARATION OF INGOTS OF URANIUM-NIOBIUM ALLOY

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Ames Laboratory
at
Iowa State College
F. H. Spedding, Director
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U N C L A S S I F I E D

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PREPARATION OF INGOTS OF URANIUM-NIOBIUM ALLOY

by

O. N. Carlson, N. Ida, D. Peterson, F. Tate and H. A. Wilhelm

ABSTRACT

A study was made of the preparation of a uranium - 10 w/o niobium alloy by the bomb reduction of a suitable form of niobium and uranium tetrafluoride with calcium. A compound with a probable formula of Na_2NbOF_5 proved to be most satisfactory as the source of niobium. High yields and good metal-slag separations were obtained. Chemical analysis and density determinations showed the composition to be 10 ± 0.5 w/o niobium. Fifteen pounds of alloy were melted in BeO and cast into a graphite mold.

INTRODUCTION

The objective of this investigation was the development of a method for preparing a uranium - 10 w/o niobium alloy of uniform composition. As reported previously¹ a few preliminary experiments were carried out in this laboratory on the preparation of some uranium-rich alloys of uranium and niobium by the bomb co-reduction of UF_4 and Nb_2O_5 with calcium. Results of these tests indicated that it might be possible to prepare the desired alloy by this method.

Some work on the preparation of the uranium - 10 w/o niobium alloy by co-melting procedures had brought out a number of difficulties which it was hoped might be eliminated by the co-reduction method. Since the co-reduction process is designed to give a uniform alloy during the reduction step, any subsequent melting and casting of the alloy would be simplified. The maximum temperature to be reached in casting would be much lower than that required for adequate alloying by co-melting. Furthermore, the time at temperature before casting would be shortened because essentially no hold is needed to obtain solution and distribution of the niobium when a co-reduced alloy is employed.

¹ P. Chiotti and O. N. Carlson, unpublished research, 1954, Ames Laboratory, Iowa State College.

EXPERIMENTAL RESULTS

A series of reductions were attempted in which Nb_2O_5 , Nb metal powder, NbCl_5 , and Na_2NbOF_5 were used in the reaction charge. Reductions were carried out in a 2 1/2 inch diameter iron pipe with a welded-in plate on one end and a threaded metal cap at the other. This reaction chamber, commonly referred to as a bomb, was lined with dolomitic oxide. The bomb was fired by heating in a gas furnace.

Attempts to prepare the 10 w/o alloy by the use of Nb_2O_5 were unsatisfactory. Poor slag-metal separation was encountered, which decreased the per cent of alloy recovered. Increasing the amount of calcium from 25 to 50 per cent excess over the stoichiometric amount did not noticeably improve the slag-metal separation. Similar results were obtained when either niobium powder or NbCl_5 was tried, although somewhat better metal-slag separations were observed when NbCl_5 was used.

It was concluded from these experiments that a halide salt of niobium was most desirable for preparing the U-10 w/o Nb alloy. The presence of a quantity of oxide in the slag reduces its fluidity and reduces the possibility of good slag-metal separation. The halide salt would also act as a thermal booster, thus raising the final temperature of the products. One such salt with which the authors had some previous experience was potassium oxyfluoniobate. This compound is easily prepared by fusing a mixture of KF , Nb_2O_5 and NH_4HF_2 in a platinum crucible at 700°C . A salt mixture having the stoichiometric composition of K_2NbOF_5 was prepared in this manner. When this compound was tried in the reduction with UF_4 , metal recovery was improved, the alloy "biscuits" were smooth, and satisfactory separation of slag and metal was observed. Analyses showed that nearly all of the niobium had alloyed with uranium. One disadvantage was the liberation of potassium in the reduction reaction which made the removal of the slag and alloy from the bomb unpleasant. In a few experiments where a graphite disc was inserted in the top of the bomb, the potassium vapors had reacted with the graphite, forming an extremely pyrophoric compound.

Therefore, a sodium salt of the oxyfluoniobate was prepared by substituting NaF for KF in the above mentioned fusion reaction. By varying the amount of NaF added, salt mixtures having the stoichiometric formulae NaNbOF_4 , $\text{Na}_3\text{Nb}_2\text{O}_2\text{F}_9$ and Na_2NbOF_5 were prepared. The best results were obtained when Na_2NbOF_5 was used in the reductions. In later experiments Na_2NbOF_5 was prepared by adding 70% HF to a mixture of NaF and Nb_2O_5 . This mixture was evaporated to dryness at 110°C and then heated to 500°C to remove any volatile products.

In the reductions employing K_2NbOF_5 , a 25% excess of calcium was used. The slag-metal separation was good and the yields were fair. In the first four reactions with Na_2NbOF_5 , a 25% excess of calcium was also used and the yields and slag-metal separation were comparable to those obtained with K_2NbOF_5 . However, by increasing the calcium excess to 50%, good yields and excellent separation of metal and slag were obtained. As shown in Table I, reductions were carried out in 2 1/2 and 4 inch diameter bombs. In each reduction the bomb was lined by jolting dolomitic oxide between a mandrel and the bomb wall. On the larger scale reductions, there was evidence of possible interaction with the dolomitic oxide. This interaction was reduced by packing a 1/4 inch layer of CaF_2 on the bottom of the bomb liner before the charge was added.

Table I

Bomb Charge Employed in Preparation of U-10% Nb Alloy

Ingredients	2 1/2" Diameter Bomb (grams added)	4" Diameter Bomb (grams added)
UF_4	650	1859
Na_2NbOF_5	147	420
Ca	336 (50% excess)	960 (50% excess)

The bomb generally required about ten minutes of heating in the furnace at $650^\circ C$ before the exothermic reaction was initiated. The instant of firing was indicated by a sudden increase in the temperature of the exterior surface of the bomb as measured by a thermocouple.

The results of several reductions are shown in Table II. As will be noted from the table, alloy recoveries in the range of 96 to 99% were obtained by this process. Chemical analyses were made on samples of alloys obtained from seven reductions. Upon adding the per cent niobium and per cent uranium for each sample, one observes that the total sum exceeds 100% in five alloys. Inasmuch as considerable care was exercised in sampling each alloy and inasmuch as all of these values are based upon the average of several analyses, the authors believe that results of the analyses for one of the components, probably uranium, are slightly high. This opinion is corroborated by the use of density measurements to estimate the alloy composition. A density versus composition curve (Fig. 1) was determined by measuring the density of standard 50 to 60 gram samples prepared by arc melting together carefully weighed amounts of uranium and niobium. As negligible weight changes were encountered in preparing these standard alloys, their compositions were assumed

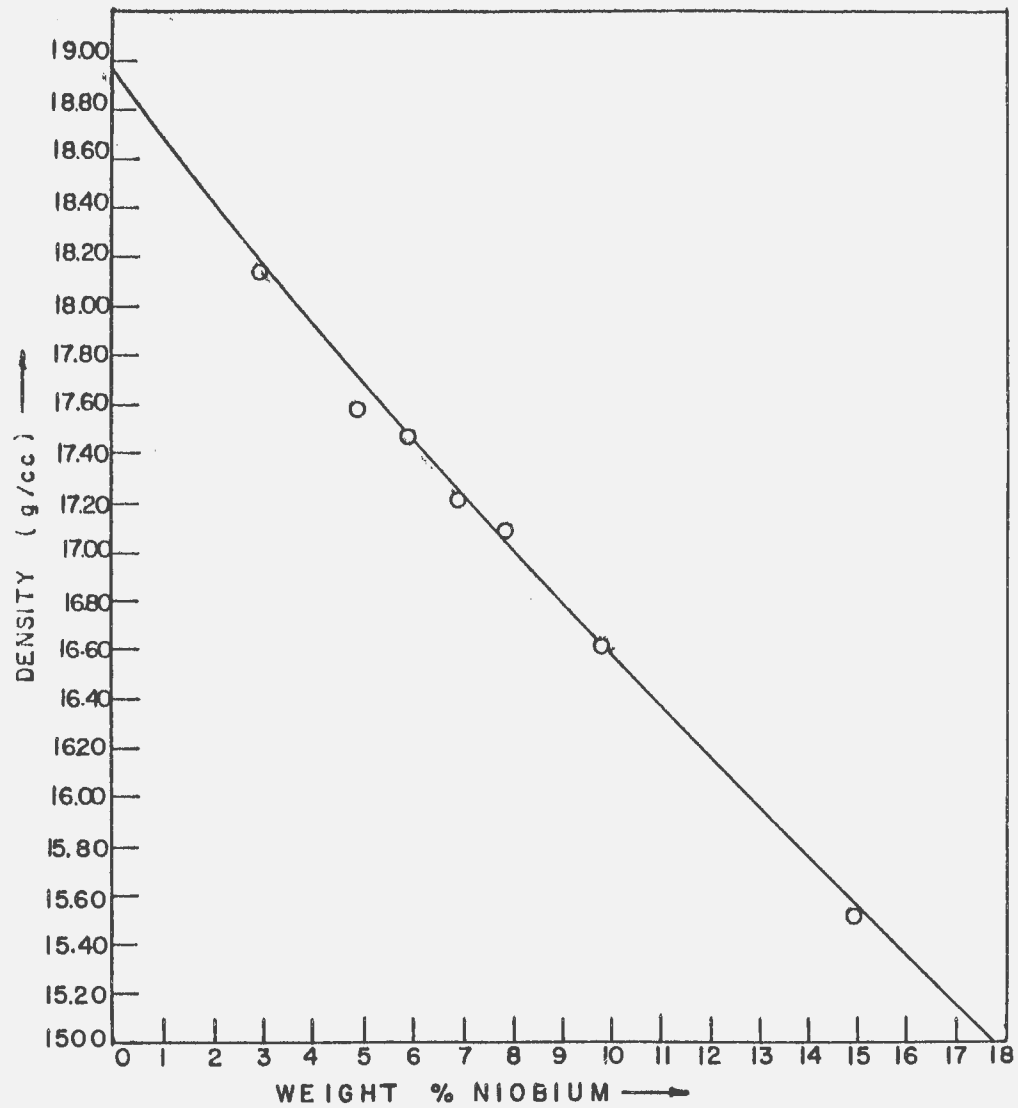


Fig. 1 - Density vs. Composition for Uranium-Niobium Alloys

Table II

Bomb Co-Reduction Data

Reduction Experiment No.	Bomb Size	% Alloy Recovered	Composition by Chemical Analysis		Composition as estimated from density w/o Nb
			w/o Nb	w/o U	
1Wn *	2½"	95%	7.85	92.56	8.45
5Wn	2½"	97.6%	10.28	90.80	10.15
6Wn	4"	98%	8.91	91.09	10.05
7Wn	4"	96%	9.96	91.87	-----
8Wn	4"	97%	9.82	89.56	9.85
9Wn	4"	97%	10.50	90.90	-----
10Wn	4"	95.9%	10.16	91.05	-----
11Wn	4"	99%	9.52	91.12	-----
12Wn	4"	95.5%	no data		
1Wn _s	2½"	97%	" "		
2Wn _s	2½"	97%	" "		

* Intended composition of this alloy was 8% Nb.

to be quite accurate. The densities were determined by use of a pycnometer in which water was used as the immersing medium. These alloys are essentially quenched from the gamma range and the density-composition curve would not be expected to apply to alloys that have been slowly cooled. Portions of four of the co-reduced alloys were arc melted, and their compositions were estimated from the curve and listed in the right hand column of Table II.

Alloy numbers 6Wn through 11Wn were pickled in a HNO_3 -HF solution preparatory to casting into ingot form. All six biscuits were placed in a BeO crucible inside a graphite cylinder which was heated by induction. The crucible was equipped with a BeO disc in the bottom which could be unseated to permit pouring of the metal at the desired temperature. Casting was carried out in a vacuum. The melting temperature of the alloy was observed by means of an optical pyrometer to be about 1500°C . The metal poured at 1675°C into a cold graphite mold. The cast ingot was about 16 inches in length, 1 1/2 inches in diameter and weighed approximately 15 pounds. The ingot was sampled by cutting disc-sections from the bottom, center and top, just below the pipe which extended down 4 inches into the casting. The results of chemical analysis and density measurements are shown in Table III. These results indicate that the composition of the ingot was nearly uniform longitudinally except for a slight increase in niobium content from bottom to top. However, these values still lie within the specified limits of 10.0 ± 0.5 w/o Nb.

Table III

Analysis of Cast Ingot

Section of Ingot	Composition by Chemical Analysis		Composition as estimated from density
	w/o Nb	w/o U	
			w/o Nb
Top	10.05	89.88	10.35
Center	10.06	91.17	10.25
Bottom	9.70	90.89	9.80

The top section had a central core about $\frac{1}{4}$ inch in diameter. This core was isolated from the rest of the section and was found to be enriched in niobium. Chemical analysis showed that it contained 11.4 w/o Nb as compared with 9.44 w/o Nb for a sample taken from near the periphery.

CONCLUSIONS

It has been demonstrated that a U-10 w/o Nb alloy can be prepared by the co-reduction of UF_4 and Na_2NbOF_5 with calcium. Homogeneous alloys close to the desired composition can be prepared in this way. These alloys may be melted in BeO and cast into ingots of fairly uniform composition. No data are reported on the amounts of such impurities as carbon, oxygen and hydrogen, nor has the method been applied to anything larger than a three-pound reduction scale. Further work is needed on the study of these and other factors before a final evaluation of the method can be made. Such studies are currently in progress.